Request for Approval of a Class 1 Permit Modification in Accordance with WIPP Permit Condition I.B.1

Waste Isolation Pilot Plant
Carlsbad, New Mexico

March 6, 2001

Request For Approval of a Class 1 Permit Modification in Accordance with WIPP Permit Condition I.B.1

Consistent with the requirements of the Hazardous Waste Facility Permit (NM4890139088-TSDF) for the Waste Isolation Pilot Plant the U.S. Department of Energy, Carlsbad Field Office is submitting to the New Mexico Environment Department (NMED) this Class 1 modification request. Specifically, this information is provided to comply with Permit Condition I.B.1 (20.4.1.900 New Mexico Administrative Code (NMAC) incorporating 40 CFR § 270.42(b).

This modification has been determined to fall into the Class 1* as indicated in 40 CFR §270.42 Appendix I, A.8. Therefore the approval of the NMED is necessary prior to implementation.

This modification is listed in Table 1. Listed information includes a reference to the applicable section of the Permit, the title of the item and the relevant permit modification category as identified in 20.4.1.900 NMAC. A more complete description of the Class 1 modification is provided in Attachment A.

The change within this modification request does not reduce the capacity of the Permittees to protect human health or the environment.

Table 1. Class 1 Hazardous Waste Facility Permit Modification

No.	Affected Permit Section	Item	Category	Attachment A Page #
1	a.1. Figure J1-2 b.1. Figure M1-13 c.1. Attach. M2- Table of Contents c.2. Figure M2-4 c.3. Figure M2-5 c.4. Figure M2-12	Eliminate the use of mini-sacks	A.8	A-1

Attachment A

Description of the Hazardous Waste Facility Class 1 Permit Modification

Item 1

Description:

Remove the magnesium oxide (MgO) mini-sacks on and around the waste containers and on the repository floor around the waste containers.

This modification is classified as a Class 1 prime modification in accordance with 20.4.1.700 NMAC (incorporating 40 CFR § 270.42, Appendix I, A.8).

Basis:

Magnesium oxide is required in the repository in order to comply with the requirements imposed by the United States Environmental Protection Agency (USEPA) in the Land Withdrawal Act (LWA Section 8g). The Department of Energy (DOE), Carlsbad Field Office (CBFO) requested approval from the USEPA on July 21, 2000 to eliminate the use of the MgO mini-sacks at the WIPP repository.

This request was based upon additional studies recently completed that indicated that the use of the mini-sacks of MgO added no benefit to the closure of the repository. Not only does the removal of the MgO mini-sacks not impact the repository environment it enhances worker safety and affords substantial efficiencies in the WIPP underground.

That request was granted by the USEPA on January 11, 2001. A copy of that approval letter is included as Attachment 1.

Discussion:

DOE has conducted a review of operational procedures required for continued safe disposal of transuranic (TRU) waste at WIPP and determined that eliminating the mini-sacks that contain magnesium oxide (MgO) would enhance worker safety at WIPP without adversely impacting repository performance.

Elimination of the mini-sacks would reduce the total mass of MgO emplaced by about 15%, however a large excess of MgO was included in the quantity specified in the Compliance Certification Application (CCA) (DOE, 1996a). Based upon the conservative assumption that all organic carbon in the waste would be converted to carbon dioxide (CO_2) by microbial degradation, the mass of MgO being emplaced was at least 1.95 times more than needed to sequester the entire resulting CO_2 inventory. In fact, it has been confirmed by recent experimental results (see Wang, 2000a: Attachment 2), that methanogenesis, which only converts half of the organic carbon to CO_2, will be the dominant biodegradation pathway in the WIPP and will account for 95% of overall carbon degradation. As a result, the quantity of MgO specified in the CCA is actually 3.7 times more than that required to sequester the entire possible inventory of CO_2. Even with the elimination of the mini-sacks, there will still be a 3.2-fold excess of MgO in the repository.

The modification provides information regarding DOE's motivation for the proposed change and an impact assessment of the change. It is concluded that eliminating the mini-sacks of MgO improves worker safety without affecting either the functionality of MgO backfill as stated in the WIPP CCA, or other components of WIPP long-term performance that EPA certified in May 1998.

Certification of the repository by the EPA for operation was based both on the information provided in the CCA and independently developed by EPA regarding the selected backfill system which consists of MgO emplaced in what would have otherwise been void space in the repository. The compliance baseline[1] for the backfill system in WIPP disposal areas calls for 85,600 tons (1.93×10^9 moles) of MgO. Approximately 15% of this total is emplaced as mini-sacks between and around waste containers. DOE recently conducted a review of WIPP's disposal operations and determined that changes to the emplacement strategy for MgO could enhance worker safety for the WIPP program, while continuing to meet all of the functional requirements associated with MgO.

Elimination of the mini-sacks will reduce the industrial hazards associated with the lifting and handling of the mini-sacks. While the bulk of the MgO backfill (85%) is contained in the super-sacks which are emplaced using a forklift, each mini-sack of MgO must be emplaced manually. This requires that personnel emplace eighteen twenty-five pound mini-sacks around the drums for each waste stack, and 11 mini-sacks against the rib at the end of each stack. This process will be repeated for the more than 108,000 estimated waste stacks (about 2,142,000 mini-sacks) to be emplaced during the life of the facility. Handling and emplacing the mini-sacks requires excessive bending and lifting, as well as climbing ladders on an uneven surface to emplace mini-sacks in the upper tiers. Each of these actions have a risk of physical injury.

Also, elimination of the mini-sacks will reduce the potential radiation exposure to workers. This exposure has been evaluated by timing the steps associated with emplacement and estimating the radiological exposure over this time period (WID, 1997). Although the total potential dose is not excessive, particularly when spread over the life of the facility, a potential reduction of dose supports the ALARA (As Low As Reasonably Achievable) requirements, which defines DOE's basic operating philosophy regarding radiation exposure. It is the installation of the mini-sacks that is responsible for most of the radiological dose associated with backfill emplacement. Elimination of the mini-sacks from the backfill system will result in the elimination of associated radiological exposure.

Recognition of the importance of worker safety issues led to an evaluation of the need for the mini-sacks in the WIPP disposal areas, and to the operational enhancements proposed in this document. The changes must meet two criteria:

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[1] Regulatory requirements and technical data implemented in support of the Compliance Certification Application. Includes all data and analyses presented to or derived by EPA [Performance Assessment Verification Test (PAVT)] in the issuance of their certification final rule.

1. Retain the function(s) of MgO as stated in the final EPA rule. This requirement ensures that performance of the repository remains unchanged from that predicted in Performance Assessment (PA) calculations conducted in support of the CCA. Therefore, no additional PA calculations are required.

2. Retain an acceptable safety factor for performance of the backfill material. This requirement provides assurance that uncertainty in geochemical processes discussed in the CCA and considered probable in the repository is sufficiently accounted for in the backfill design and associated PA calculations.

Demonstration that these criteria are met ensures that the proposed elimination of mini-sacks does not constitute a change to activities pertaining to the disposal system that differs significantly from the previously referenced CCA.

References

U.S. Department of Energy. 1996a. 40 CFR 194. Compliance Certification Application for the Waste Isolation Pilot Plant. Chapter 1-9.

Wang, Y. 2000a. Memorandum to Bryan A. Howard. January 5, 2000. “Methanogenesis and Carbon Dioxide generation in the Waste Isolation Pilot Plant”.

Westinghouse Electric, Waste Isolation Division. (WID). 1997. WIPP Radiological Control Position Paper 97-05: “Dose Assessment for Hand Emplacement of MgO Sacks Around CH Waste 7-Packs at the Waste Isolation Pilot Plant”, April. 1997.

Revised Permit Text:

a.1. Figure J1-2

Revised Figure J1-2 is shown in Attachment B of this modification package

b.1. Figure M1-13

Revised Figure M1-13 is shown in Attachment B of this modification package

c.1. Attachment M2 – Table of Contents

List of Figures

Figure **Title**

c.2. Figure M2-4 - Waste Containers With Mini Sacks Attached

Figure M2-4 has been deleted

c. 3. Figure M2-5 - Backfill Sacks Emplaced in a Room

Revised Figure M2-5 is shown in Attachment B of this modification package

c. 4. Diagram M2-12 - Facility Surface and Underground CH Transuranic Mixed Waste Process Flow Diagram

Revised Diagram M2-12 is shown in Attachment B of this modification package

Attachment B

Figure J1-2

Standard Waste Box and Seven Pack Configuration

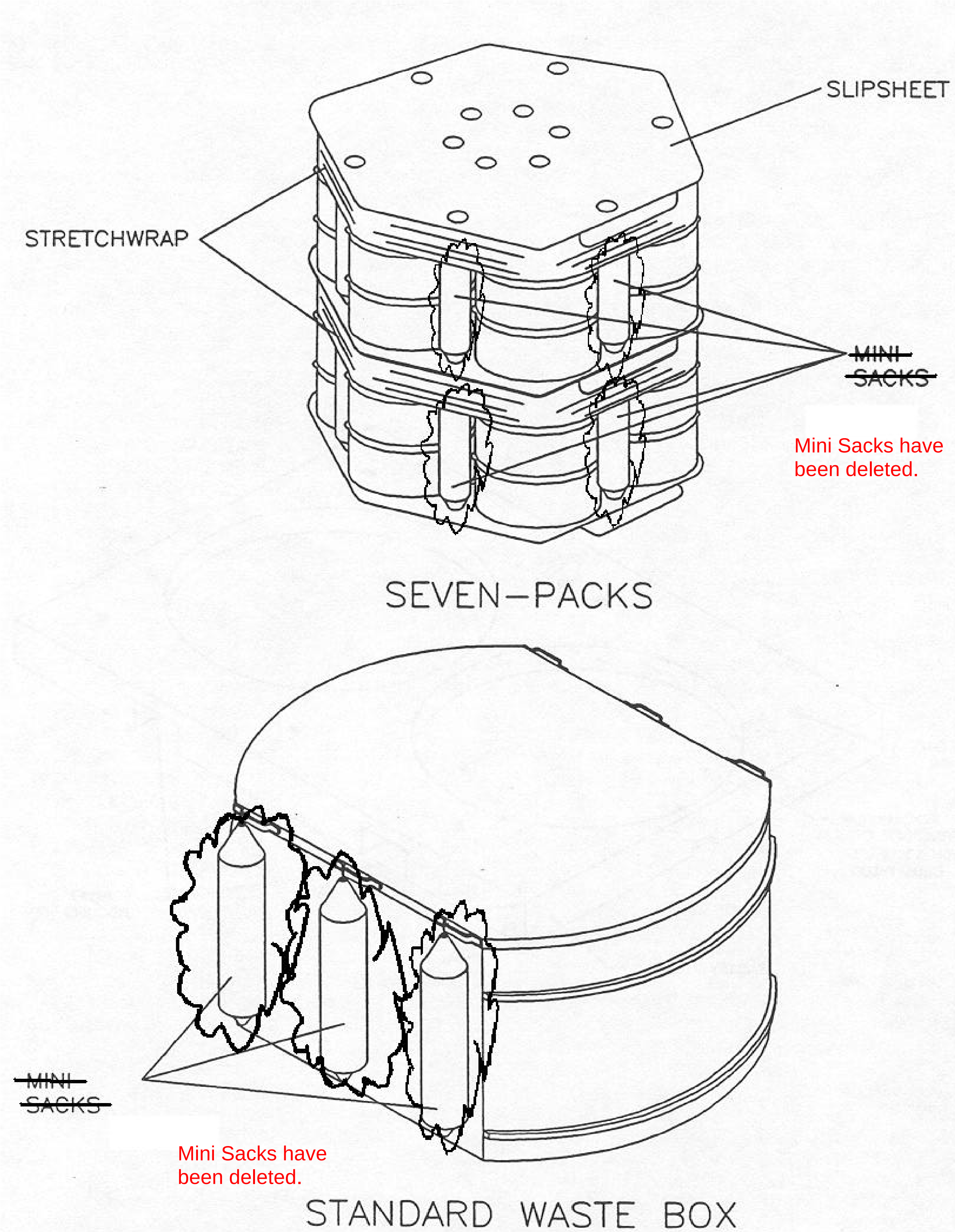

Figure J1-2
Standard Waste Box and Seven Pack Configuration

Figure M1-13

WIPP Facility Surface and Underground CH Transuranic Mixed Waste Process

Flow Diagram

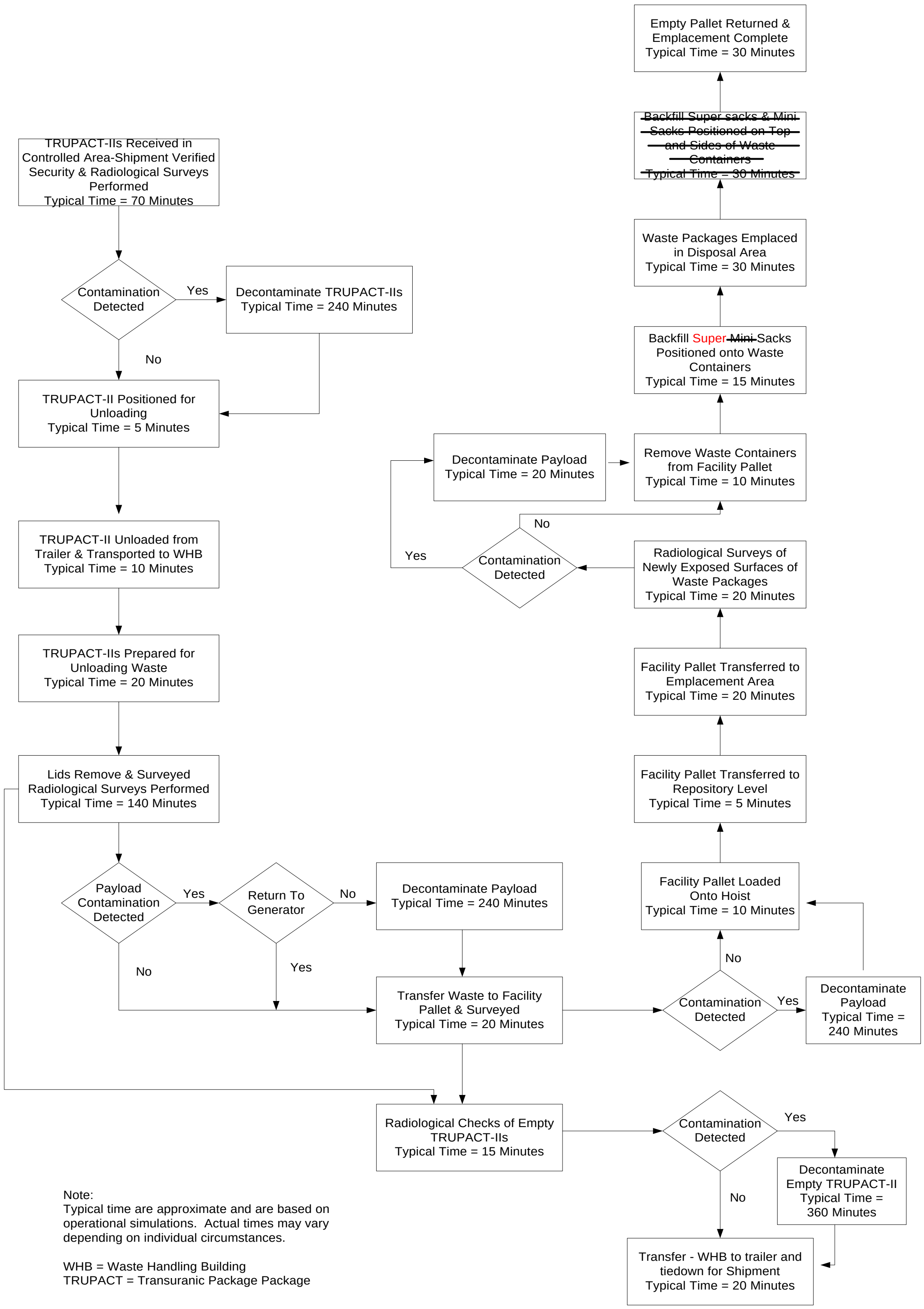

Figure M1-13
WIPP Facility Surface and Underground CH Transuranic Mixed Waste Confirmation Process Flow Diagram

Figure M2-5

Backfill Sacks Emplaced in a Room

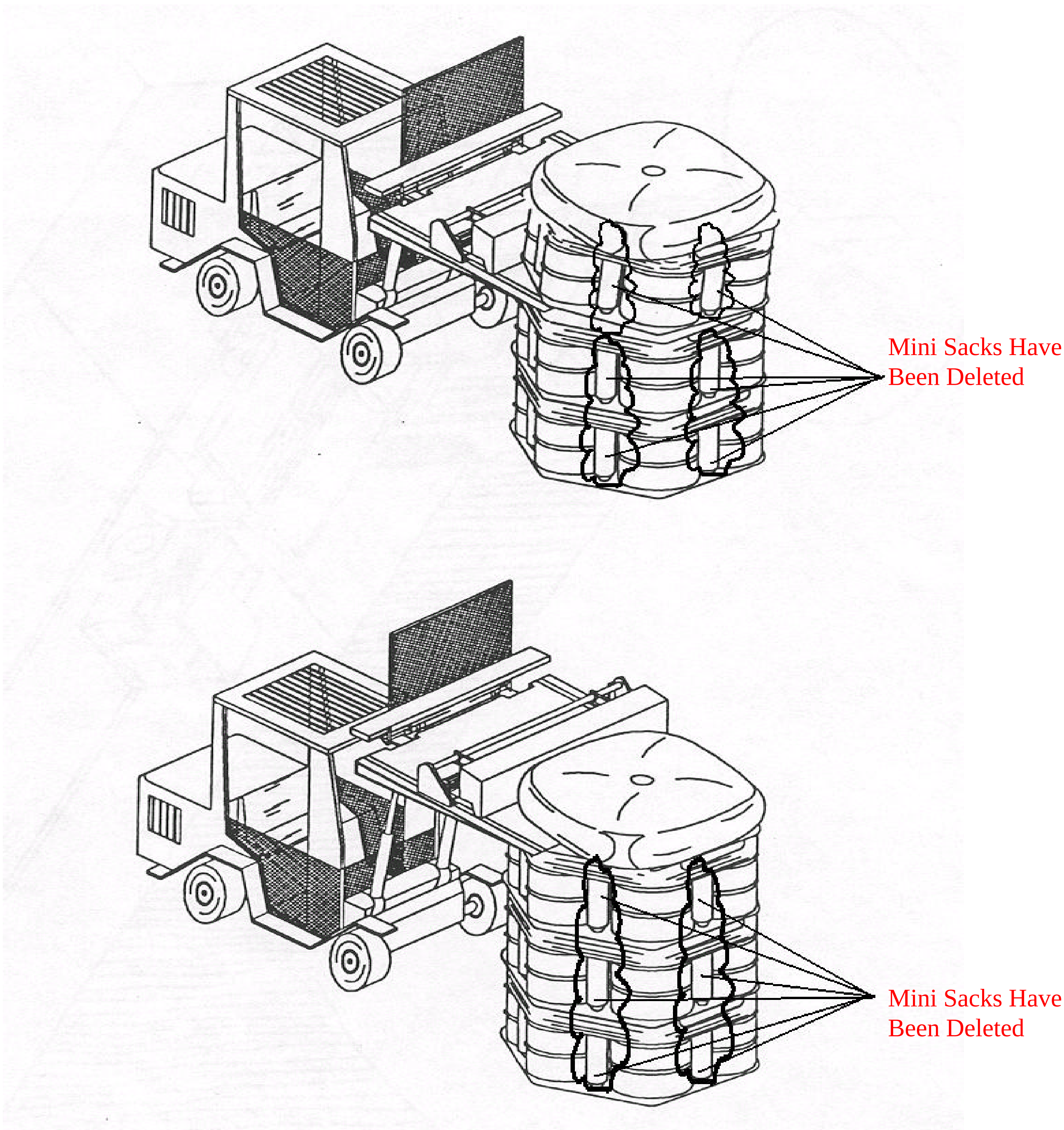

Figure M2-5
Backfill Sacks Emplaced in A Room

Figure M2-12

WIPP Facility Surface and Underground CH Transuranic Mixed Waste Process Flow Diagram

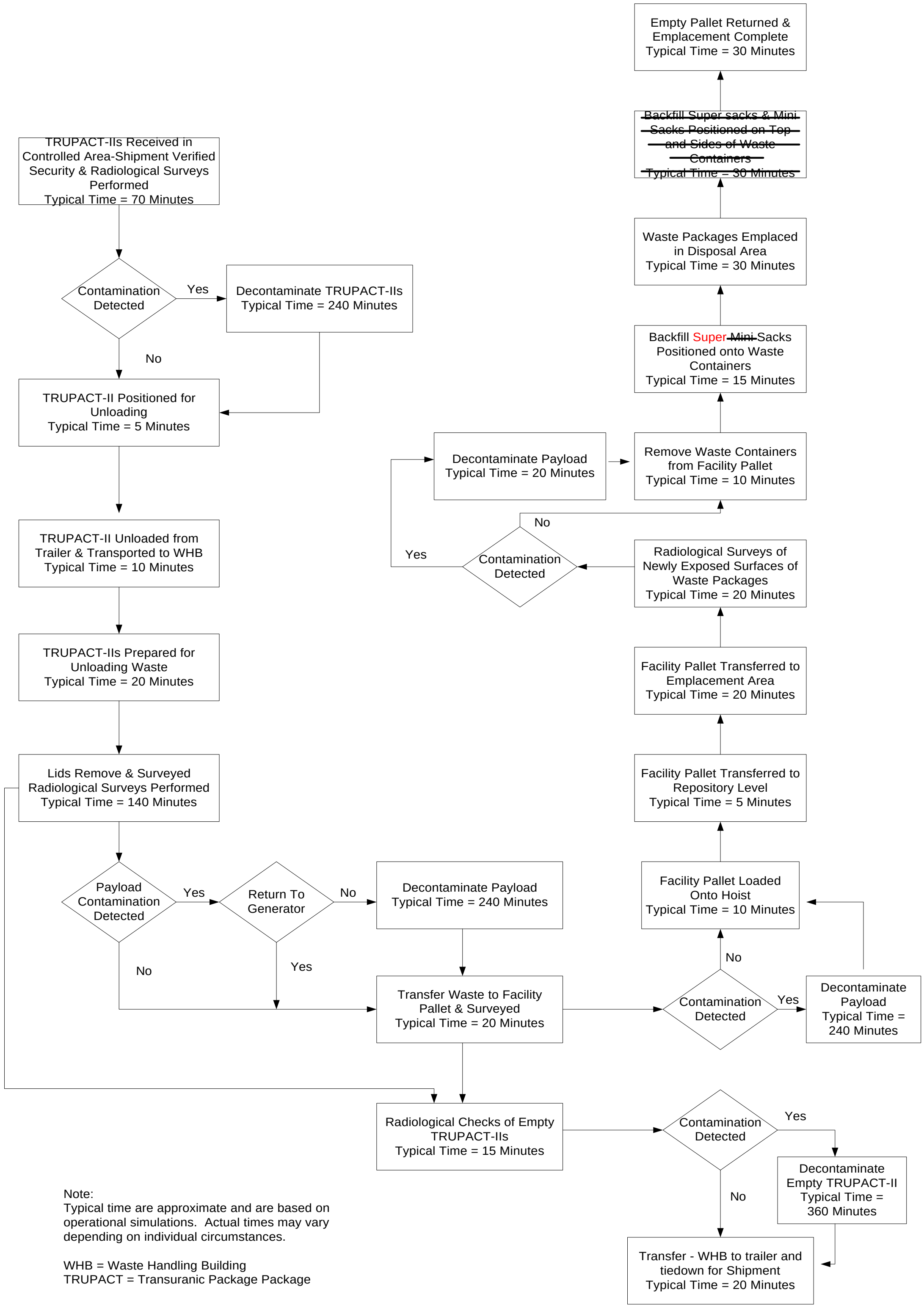

Figure M2-12
WIPP Facility Surface and Underground CH Transuranic Mixed Waste Confirmation Process Flow Diagram

Attachment 1

USEPA Approval Letter for Removal of MgO Mini-Sacks

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JAN 11 2001

OFFICE OF
AIR AND RADIATION

Dr. Ines Triay
Carlsbad Field Office
Department of Energy
P.O. Box 3090
Carlsbad, NM 88221

Dear Dr. Triay:

Thank you for your letter dated July 21, 2000, in which you requested the Environmental Protection Agency's (EPA's) approval for the elimination of magnesium oxide (MgO) mini-sacks from the Waste Isolation Pilot Plant (WIPP). The elimination of the mini-sacks would result in a fifteen percent reduction in the total amount of MgO that must be placed in the WIPP, in accordance with the WIPP Compliance Certification Application and EPA's certification decision.

We have reviewed your request and agree that this change, which you have proposed to improve operational safety, will not significantly impact the WIPP's long-term performance (see the enclosed report). The quantity of MgO that the Department of Energy (DOE) is required to place in the WIPP is expected to prevent or delay substantially the movement of radionuclides to the accessible environment. Therefore, we approve your proposal.

We will place our report and your proposal in our public docket. We expect that DOE will track and report on this change in accordance with our guidance to DOE on recertification.

Sincerely,

Frank Marcinowski, Acting Director
Radiation Protection Division

Enclosure

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[illegible]	[illegible]	JAN 22 2001	[illegible]

MgO Mini-sack Review

1.0 Introduction

This report summarizes EPA's review of DOE's proposal to eliminate magnesium oxide (MgO) mini-sacks from the Waste Isolation Pilot Plant (WIPP). This report responds to a formal request from Dr. Ines Triay of DOE dated July 21, 2000 (See Attachments 1 to 4). It includes information obtained during a DOE/EPA technical exchange meeting held in Washington, DC, on April 12-13, 2000 (See Attachment 5).

2.0 Overview of DOE Proposal

DOE requested that EPA approve the elimination of approximately 15% of the total quantity of MgO in the repository by removing backfill mini-sacks placed on and around waste drums and waste boxes (see Table 1). The backfill to be eliminated would be eighteen 25-lb bags (mini-sacks) of MgO around each waste stack and the mini-sacks from the floor around the waste containers. DOE states this proposal would "significantly enhance worker safety at the WIPP without adversely impacting repository performance" (see Attachment 2).

Table 1: DOE's Calculation of Excess of MgO

Case	Quantity	Value
Assume all organic carbon; cellulosics, papers, and rubbers, reacts to form CO_2	Moles CO_2	Maximum of 9.85×10^8 moles of CO_2 generated
	Original planned MgO in repository	85,600 tons @ 40.3 gm/mole = 1.93×10^9 moles
	Original CCA excess of MgO	1.95 times
	15% reduction	74,000 tons @ 40.3 gm/mole = 1.65×10^9 moles
	New MgO excess	1.67 times

In the Compliance Certification Application (CCA) DOE proposed, and EPA subsequently approved, the emplacement of approximately 85,600 tons of MgO as an engineered barrier to achieve two purposes: remove carbon dioxide (CO_2) gas created by microbial degradation of cellulosics, papers, and rubbers, and increase the pH in the repository to lower the solubility of dissolved actinides. As noted in DOE's letter of July 21, the amount of MgO presently planned for emplacement is almost twice that needed to sequester the CO_2 generated if <u>all</u> of the organic waste was converted to CO_2 (this constitutes a bounding assumption).

The primary benefits of this change would occur during the operational period by enhancing worker safety and decreasing cost. Decreasing the amount of MgO by 15% is not expected to significantly affect long-term repository performance, as discussed in Section 3.0 below.

3.0 Analysis

We reviewed relevant information in the CCA (especially Appendix BACK), EPA's Compliance Application Review Documents (CARDs) and Technical Support Documents (TSDs) for the certification rulemaking, the results of the CCA Performance Assessment (PA) and Performance Assessment Verification Test, and the DOE support documents submitted with the July 21st letter (Attachment 2).

Also, during a WIPP site visit in June following a technical meeting in Carlsbad, NM, EPA staff observed waste containers that had been placed in Panel 1 and noted that MgO mini-sacks were attached to containers and lay on the floor around the perimeter of the waste containers. Agency staff also evaluated the methods used to attach mini-sacks to waste containers. We found that DOE accurately represented the steps required to attach mini-sacks to the waste containers and the worker safety considerations involved in this activity (see Attachment 5).

DOE's conceptualization of MgO performance in the repository was very conservative. In CARD 44: Engineered Barriers, the Agency stated:

> ". . . the reaction of MgO to brucite would consume water, an added benefit for which DOE did not take credit in the PA. Additionally, other mineral species that may form (dypingite ($Mg_3(CO_3)_4(OH)_2 \cdot (5H_2O)$) and/or nesquehonite ($MgCO_3 \cdot 3H_2O$) consume five and time times as much water, respectively. These factors constitute a conservative approach that accounts sufficiently for uncertainties in geochemical processes that may occur in the disposal system" (p. 44-9).

The elimination of mini-sacks does not impact the CCA or PAVT results because DOE proposes to reduce only excess MgO, which was not used in the performance calculations. Compliance with EPA's containment requirements is not altered because there would still be a large excess of MgO relative to any potential evolved carbon.

The ability of the MgO remaining in super-sacks to react with brine in the repository is important if the mini-sacks are eliminated. Attachment 4 concludes that molecular diffusion alone can effectively mix brine with MgO from degraded super-sacks in a repository that has experience salt creep closure. Super-sacks of MgO will break open as the height of the repository compresses from 3 meters to .8 to 1.4 meters, mixing the MgO with the degraded waste and waste containers. If brine is introduced into the disposal rooms MgO will be readily available to react chemically. We reviewed DOE's calculations and agree these processes will function as expected and sufficient MgO will be available to react.

4.0 Conclusion

In conclusion, we determined that the analysis of the effectiveness of MgO backfill, as described in EPA's certification decision, would not be compromised by the elimination of the mini-sacks:

- MgO is still expected to remove CO_2 and to affect pH and actinide solubility
- the excess amount of MgO proposed for emplacement ensures that adequate MgO will still be available to provide expected chemical effects
- the plan for emplacing MgO remains feasible.

The elimination of the MgO mini-sacks is not significant to long-term repository performance. DOE's proposal to decrease the amount of MgO in the WIPP by 15% by eliminating the MgO mini-sacks is acceptable.

Attachment 2a

Methanogenenesis and Carbon Dioxide Generation at the Waste Isolation Pilot Plant (WIPP)

Sandia National Laboratories

Operated for the U.S. Department of Energy by Sandia Corporation

Carlsbad, NM 88220

date: January 5, 2000

to: Bryan A. Howard (Org. 6821)

from: Yifeng Wang (Org. 6821)

subject: Methanogenesis and Carbon Dioxide Generation at the Waste Isolation Pilot Plant (WIPP)

INTRODUCTION

Microbial gas generation will have a significant impact on the near field chemistry of the Waste Isolation Pilot Plant (US DOE, 1996, appendix SOTERM). To mitigate the effect of microbially-generated carbon dioxide on actinide solubility, the Department of Energy (DOE) decided to emplace 77,640 metric tons (equivalent to 2 x 10^9 moles) of MgO as a backfill into the WIPP (Bynum et al., 1998). This total amount of MgO was estimated based on the following assumptions (Peterson, 1996):

(1) Organic materials (cellulosics, plastics, and rubber) will be completely degraded over 10,000 years,
(2) one mole carbon (C) in organic materials will be converted to one mole of carbon dioxide (CO_2),
and
(4) there will be sufficient space for the emplacement of MgO.

The first two assumptions are overly conservative. This memorandum intends to demonstrate that the conservatism associated with the second assumption conflicts with current data showing that methanogenesis will be a dominant biodegradation pathway in the WIPP repository. Therefore, at most one half of organic carbon can possibly be converted to CO_2.

METHANOGENESIS IN WIPP

Cellulosics, plastics, and rubbers have been identified as major organic materials to be emplaced in the WIPP repository (DOE/CAO, 1996) and could be degraded by microbes in 10,000 years (Brush, 1995). Depending on the availability of electron acceptors (e.g., NO_3^-, and SO_4^{2-}), microorganisms will degrade organic materials by the following reaction pathways (Brush, 1995):

$$C_6H_{10}O_5 + 4.8\,H^+ + 4.8\,NO_3^- \rightarrow 7.4\,H_2O + 6\,CO_2 + 2.4\,N_2 \quad (1)$$
$$C_6H_{10}O_5 + 6\,H^+ + 3\,SO_4^{2-} \rightarrow 5\,H_2O + 6\,CO_2 + 3\,H_2S \quad (2)$$
$$C_6H_{10}O_5 + H_2O \rightarrow 3\,CH_4 + 3\,CO_2. \quad (3)$$

The reaction pathways of aerobic respiration, Mn(IV) and Fe(III) dissimilatory reduction are ignored here, because the quantities of O_2, Mn(IV) and Fe(III) initially present in the repository will be negligible relative to the other electron acceptors. The above reactions generally proceed sequentially from Reaction (1) to (3) according to a decreasing order of energy yields of the reactions (e.g., Berner, 1980; Criddle et al., 1991; Chapelle, 1993; Wang and Cappellen, 1996; Hunter et al., 1998). It is important to notice that methanogenesis produces only half mole of carbon dioxide from one mole of organic carbon.

Aside from theoretical consideration of the energetic perspective, the biodegradation sequence summarized above is widely observed in the nature (e.g., Berner, 1980; Criddle et al., 1991; Chapelle, 1993). The occurrence of methanogenesis following denitrification and sulfate reduction is commonly observed in marine sediments, especially in coastal sediments, which receive a high input of organic matters (e.g., Schlesinger, 1997, p.284). Methanogenesis can be a dominant biodegradation process in many terrestrial geochemical systems such as freshwater wetlands and lakes, where the supply of sulfate is usually limited (e.g., Schlesinger, 1997, p.237). Methanogenesis is observed to occur in either pristine or contaminated groundwater systems (e.g., Chapelle, 1993). Methane generation in landfills is a typical example (Baedecker and Back, 1979). In all these systems, the occurrence of methanogenesis follows, with no exception, the biodegradation sequence summarized by Reaction (1) to (3). Therefore, it follows that methanogenesis is likely to occur in the WIPP repository after all nitrate and sulfate are consumed. It is worth noting that Nirex has included methanogenesis in the performance assessment for low-level waste disposal (Nirex, 1997).

In the previous gas generation experiments, which were used to derive gas generation parameters for the WIPP Compliance Certification Application (CCA) (Wang and Brush, 1996), cellulose samples were incubated for 1228 days with microorganisms collected from WIPP-relevant environments (Francis et al., 1997). At the time of the CCA calculations no methane production was detected in any of those samples. There are two possible explanations for the absence of methane production. The first possibility is that microbial degradation in the samples had not reached the methanogenesis stage, due to a relatively short incubation time and also because of high nitrate or sulfate concentration in the brine. If this is the case, methane would be produced after the samples are incubated for a long enough time and all nitrate and sulfate in the samples are consumed. The second possibility is the lack of active methanogenic microbes in the samples. If this were the case, no methane would be produced even if the samples were incubated for a very long time. To test these possibilities, A. J. Francis and J. Gillow at Brookhaven National Laboratory (BNL) have conducted more headspace gas measurements on samples that have been preserved from the previous WIPP gas generation program (See WIPP Test Plan TP99-01). The objective of these measurements was to check if methane had been produced in those samples after extended incubation (~ 7.5 years). Methane was analyzed in selected brine-inundated samples and the results are summarized in Table 1 (Francis and Gillow, 2000).

Methane was produced in most anaerobic samples except those with excess nitrate. Nitrous oxide was detected in the headspace of samples containing excess nitrate. The lack of methane production in samples amended with nitrate-compounds indicates the inhibitory effect of nitrate on methanogenic bacterial activity. In fact, most of the methane detected was in samples that were not amended with any nitrate-containing compounds (NH_4NO_3, KNO_3) at all (unamended and unamend/inoculated samples). This supports the hypothesis of biogenic origin of methane in these samples. Of the initially aerobic samples, only two treatments contained methane (unamended and unamended/inoculated (without bentonite)). In all of the other initially aerobic treatments, the combination of oxygen, nitrate-compounds, and other alternate electron acceptors (Fe^{3+} provided by bentonite) may have an inhibitory effect on methanogenesis.

Table 3. Methane analysis of inundated cellulose samples. All samples have been corrected for the gas produced in control treatments (without cellulose). nd = not detected.

Sample	1228 Days (nmol g^{-1} cellulose)	2718 Days (nmol g^{-1} cellulose)
Anaerobic		
Unamended	nd	3.92 ± 0.27
Unamended/Inoculated	nd	4.03 ± 1.38
Amended/Inoculated	nd	0.85 ± 0.7
Amended/Inoc. + Exc. Nitrate	nd	nd
Anaerobic + Bentonite		
Unamended	nd	3.84 ± 0.40
Unamended/Inoculated	nd	3.52 ± 0.20
Amended/Inoculated	nd	1.12 ± 0.03
Amended/Inoc. + Exc. Nitrate*	nd	nd
Initially Aerobic		
Unamended	nd	1.25 ± 0.29
Unamended/Inoculated	nd	1.10 ± 0.13

Although the quantities of methane detected are small, the new measurements have demonstrated that the absence of methane production in the previous measurements was due to the inhibitory effect of nitrate or sulfate and the insufficient incubation time period. Based on the experimental data and the observations on natural systems, it can be concluded that methanogenesis will take place in the WIPP repository after microorganisms consume all nitrate and sulfate. In the next section, based on waste inventory estimates, it is further demonstrated that methanogenesis can eventually become a dominant reaction pathway in the WIPP repository.

AMOUNT OF CARBON DIOXIDE TO BE GENERATED IN WIPP

Inventories of organic materials and electron acceptors (NO_3^- and SO_4^{2-}):

Based on the Transuranic Baseline Inventory Report (DOE/CAO, 1996), the total equivalent cellulosics to be emplaced in the WIPP is estimated to be 2.656×10^7 kg, equivalent to 9.84×10^8 moles of C (Peterson, 1996). The total amounts of nitrate and sulfate in the waste are estimated to be 1.6×10^6 kg and 6.3×10^5 kg, respectively, and equivalently 2.6×10^7 moles of NO_3^- and 6.6×10^6 moles of SO_4^{2-} (DOE, 1996, p. B6-1; Wang and Brush, 1996, p.14). A certain amount of sulfate can be brought into the repository by brine inflow; however, this amount of sulfate is estimated to be less than 4×10^6 moles (Wang and Brush, 1996). Therefore, the total amount of sulfate to be present in the repository is estimated to be 1×10^7 moles.

Fraction of methanogenesis:

As mentioned above, the biodegradation of organic materials in the WIPP will proceed sequentially from Reaction (1) to (3). The fractions of individual degradation pathways can be calculated as follows:

Molar fraction of organic carbon degraded via denitrification
= 1.25 x moles of nitrate/moles of organic carbon
= $1.25 \times 2.6 \times 10^7 / 9.84 \times 10^8 = 3.3\%$
Molar fraction of organic carbon degraded via sulfate reduction
= 2 x moles of sulfate/moles of organic carbon
= $2 \times 1 \times 10^7 / 9.84 \times 10^8 = 2\%$
Molar fraction of organic carbon degraded via methanogenesis
= 1 – molar fractions of both denitrification and sulfate reduction
= $1 - 3.3\% - 2\% = \sim 95\%$.

Therefore, based on the currently inventory estimates, methanogenesis will account for 95% of overall organic carbon degradation.

Total possible quantity of CO_2 to be generated:

Using the fractions of biodegradation pathways calculated above, it can be estimated that one mole of organic C will be converted to $(1 - 95\%) + 95\% \times 0.5 = 0.525$ mole of CO_2. Accordingly, the total possible quantity of CO_2 to be generated in the repository is estimated to be $0.525 \times 9.84 \times 10^8 = 5.17 \times 10^8$ moles, which is about 47.5% less than that estimated for the CCA (Peterson, 1996).

Given the fact that metal corrosion in the repository will generate a significant quantity of H_2, another methanogenesis pathway may also exist, in which methanogenic microbes use both CO_2 and H_2 as substrates to produce methane: $CO_2 + 4H_2 = CH_4 + H_2O$ (Brush, 1995, p.E-16). As a result, the conversion ratio of organic carbon to CO_2 can be even smaller. Because of lack of experimental data, the second methanogenesis pathway is ignored here.

CONCLUSION

Methanogenesis will be a dominant biodegradation pathway in the WIPP repository and account for 95% of overall organic carbon degradation. Based on the current waste inventory, it is estimated that one mole of organic C will be converted to 0.525 mole of CO_2. Accordingly, the total quantity of CO_2 potentially to be generated in the repository is calculated to be 5.17×10^8 moles, which is about 47.5% less than that estimated for the CCA (Peterson, 1996).

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Attachment 2b

Effectiveness of Mixing Processes in the Waste Isolation Pilot Plant Repository

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subject: Effectiveness of Mixing Processes in the Waste Isolation Pilot Plant Repository

MgO backfill is being used in the Waste Isolation Pilot Plant (WIPP) as a chemical control agent to mitigate the effect of microbial CO_2 generation on actinide mobility in a post-closure repository environment. MgO is emplaced as super-sacks on the top of waste container stacks and as mini-sacks between and around waste containers. To enhance worker safety, the Department of Energy (DOE) proposes to eliminate the emplacement of MgO mini-sacks. This memorandum supports the DOE's assessment that the elimination of MgO mini-sacks will not impact MgO/brine accessibility in the WIPP and therefore the functionality of MgO as a chemical control will remain effective as stated in the Compliance Certification Application (CCA). Using a bounding calculation, the memo demonstrates that molecular diffusion alone will be sufficient to mix brines with MgO backfill in the repository without the presence of MgO mini-sacks.

In the following bounding calculation, only molecular diffusion is considered. The diffusion of a chemical species in a porous medium can be described by Fick's equation (e.g., Richardson and McSween, 1989, p.132):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X}\left(D_{eff}\frac{\partial C}{\partial X}\right) \qquad (1)$$

where C is the concentration of the diffusing chemical species; t is the time; X is the distance; and D_{eff} is the effective diffusivity of the chemical species in a given porous medium. D_{eff} is related to the porosity (ϕ) of the medium by (e.g., Oelkers, 1996):

$$D_{eff} = \phi^2 D \qquad (2)$$

where D is the diffusivity of the species in pure solution. The D values for most aqueous species at room temperatures fall into a narrow range, and 10^{-5} cm^2/sec is a good approximation (e.g., Richardson and McSween, 1989, p.138). From the CCA calculations (Bean et al., 1996, p.7-29; WIPP PA Department, 1993, equation B-8), the porosity in the WIPP waste panels after room closure is calculated to be 0.4 to 0.7. From Equation (2), the effective diffusivity D_{eff} in the waste is estimated to be $2 \sim 5\text{x}10^{-6}$ cm^2/sec ($\approx 6 \sim 16\text{x}10^{-3}$ m^2/year).

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Given a time scale of T, the typical diffusion penetration distance (L) can be determined by scaling Equation (1):

$$L = \sqrt{D_{eff} T}\,. \qquad (3)$$

Using Equation (3), the diffusion penetration distance in the WIPP can be calculated as a function of diffusion time, as shown in Figure 1.

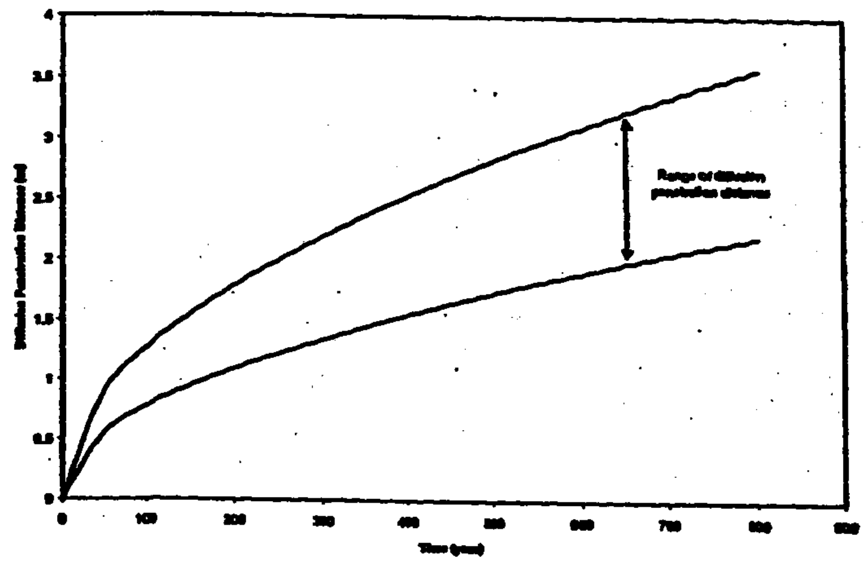

Figure 1. Diffusion penetration distance in the WIPP as a function of diffusion time

The average time for a brine pocket to remain in a waste panel after it enters the repository is characterized by a so-called mean residence time ($T_{residence}$), which can be calculated by:

$$T_{residence} = \frac{V_\phi}{F} \qquad (4)$$

where V_ϕ is the pore volume in a waste panel; and F is the rate of brine flow up to the Culebra formation through a borehole. From the CCA calculations, the pore volume in a waste panel after room closure ranges from 2,500 to 7,000 m^3 (Helton et al., 1998, p.8-50), and the maximum flow rate is 5.5 m^3/year (Helton et al., 1998, p.8-69). Using these values, $T_{residence}$ is estimated to be > 450 years. Over this time scale, according to Equation (3) and Figure 1, molecular diffusion alone can mix brine composition effectively at least over a distance of 1.6 m.

The height of waste stacks in the repository after room closure (h) can be calculated by:

$$h = \frac{h_0(1-\phi_0)}{1-\phi} \qquad (5)$$

where h_0 and ϕ_0 are the initial height of waste stacks and the initial porosity of wastes, which are assumed to be 4 m and 0.88, respectively, in the CCA. For $\phi = 0.4 - 0.7$, h is estimated to be 0.8 to 1.4 m, which is less than the calculated diffusion penetration distance. Since MgO super-sacks are directly placed on the top of waste stacks in the current waste emplacement configuration, it can be concluded that molecular diffusion alone can effectively mix brines with super-sack MgO (in a vertical direction) without the presence MgO mini-sacks. In other words, the elimination of MgO mini-sacks will not affect MgO accessibility by brine in the WIPP.

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